



Replacement Sheets
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A cleaning composition for substantially complete removal of both a low-k layer and photoresist layer can also be prepared with an organic fluoride such as hydrogen fluoride pyridinium combined with an inorganic acid such as sulfuric acid. A preferred composition comprises an about 1:5 ratio (v/v) of hydrogen fluoride pyridinium and 90 % sulfuric acid (H₂SO₄), and/or other inorganic acid, or about 13 to about 19 % by volume hydrogen fluoride pyridinium and about 80 to about 86 % by volume of 90% H₂SO₄ and/or other inorganic acid, to provide a rapid rate of removal of the photoresist layer and a rate of removal of the dielectric layer at about 700 angstroms per minute.

B₁ A second embodiment of a cleaning composition according to the invention, and a method for its use is described with reference to **FIGS. 2A-2B**. The wafer 30 to be cleaned includes a substrate 12, for example, a silicon substrate, and a surface 14. Overlying the surface 14 of the substrate 12 is an unmasked low-k dielectric film or layer 16 having a thickness T₁. According to the method, the cleaning composition is applied to the wafer 30 for removal of at least a portion of the low-k dielectric layer 16 from the surface 14 of the silicon-comprising substrate 12. **FIG. 2B** depicts the portion of the wafer 30 after cleaning. As depicted, the thickness T₁, of the low-k dielectric layer 16 has been reduced to thickness T₂ by the removal process. The low-k dielectric layer 16 can also be completely removed to produce a hydrophobic, oxide-free silicon surface 14, as depicted in **FIG. 1B**.

The foregoing cleaning compositions can be formulated according to the invention to provide removal of at least a portion of the low-k dielectric layer 16 from the surface of a semiconductor wafer at a rapid rate of removal (>1000 angstroms per minute) or a more controlled low to moderate rate of removal (about 50 to about 1000 angstroms per minute). A slow and controlled removal of low-k dielectric films is desirable in cases where removing the low-k dielectric material too quickly from the wafer leads to inadequate process control and causes difficulty in process integration. This is important when the objective is to remove small amounts of the low-k dielectric, such as from a silicon contact area. For example, in a post-etch cleaning, it is desirable to selectively remove a low-k dielectric material from a wafer at a slow and controlled rate in order to remove a small amount of the dielectric material from an etched

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feature and leave the bulk of the film intact. In that case, a preferred etchant composition is one that is formulated with a dilute HF ratio.

B₂ The compositions can be used to selectively remove all or a portion of a masked low-k dielectric layer while leaving the photoresist mask essentially intact. Such a composition is useful where wet patterning is required (rather than RIE). The composition is formulated to provide an etch selectivity ratio of about 50:1 to about 1000:1 (low-k dielectric:photoresist) whereby the low-k dielectric material is selectively removed without attacking the photoresist or other organic material.

Another embodiment of a cleaning composition according to the invention, and a method for its use to remove photoresist from a wafer surface while leaving an underlying low-k dielectric layer essentially intact on the wafer surface, is described with reference to **FIGS. 3A-3B**. A portion of a wafer 40 is shown which includes a substrate 12, for example, a silicon substrate, with a surface 14. A layer or film of a low-k dielectric material 16 overlies the surface 14 of the substrate 12. Overlying the low-k dielectric layer 16 are portions of a photoresist mask 18. According to the method, a cleaning composition is applied to a wafer 40 to provide selective removal of substantially all of the photoresist mask layer 18, while leaving the underlying layer of low-k dielectric layer 16 essentially intact. **FIG. 2B** depicts the portion of the wafer 40 after cleaning, with the photoresist layer 18 having been completely removed by the cleaning process with the low-k dielectric material remaining on the wafer substrate 12.

B₃ This cleaning method is particularly useful for removing a photoresist layer after an etch processing step, or in a rework application to remove a misaligned resist mask. The composition is formulated to provide an etch selectivity ratio of about 200:1 (photoresist:low-k dielectric) in which the photoresist material is selectively removed at about 200 angstroms/minute without substantially attacking the low-k dielectric material, or a rate of removal of up to about 1 angstrom/minute.

A useful composition for the sole removal of a photoresist mask layer or other organic layer overlying a low-k dielectric layer comprises an aqueous solution of an inorganic fluorine-comprising compound and a major amount of an organic acid such as a 50% citric acid, with a pH of about 3 to about 4. A preferred composition comprises an about 1:100 (v/v) of an
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inorganic fluorine-comprising compound and an about 20 to about 60 %, preferably about 40 % to about 50 %, aqueous solution of an organic acid. Preferably, the inorganic fluorine-comprising compound is included in an amount of up to about 2 % by volume, preferably about 0.5 % to about 1.5 % by volume, and the organic acid is included in an amount of up to about 5 99.5 % by volume, preferably about 98.5 % to about 99.5 % by volume, based on the total volume of the composition, with a pH of about 3 to about 3.5. A preferred composition comprises an about 1:100 ratio of 49 % HF and 50 % citric acid and/or other organic acid, which provides a rate of removal of the photoresist layer at about 400-600 angstroms per minute with an etch selectivity (polymeric photoresist material:low-k material) of at least about 200:1.

10 To clean a wafer surface according to the invention, the wafer is placed in contact with an appropriately formulated cleaning composition to remove the desired layer or layers at a desired rate of removal. The cleaning composition can be applied using a conventional wet chemical application technique as known and used in the art. For example, one or more wafers can be placed vertically in a carrier or boat and then submerged in a recirculating bath of the cleaning 15 composition, with or without agitation for about 5-10 minutes, depending on the thickness of the layer to be removed. The cleaning composition can also be sprayed onto the surface of the wafer. Preferably, a substantially constant concentration of the reactive components of the cleaning composition is brought into contact with the wafer surface so that a uniform rate of removal can be maintained to allow for process uniformity and the desired extent and 20 completeness of removal.

In the cleaning of a wafer, the cleaning composition can be used at a temperature of about 15°C. to about 30°C., preferably at about 15°C. to about 30°C. High temperatures of about 40 to about 60° C. can be typically used to achieve faster etch rates. In a selective removal of a photoresist mask or other organic material and not a low-k dielectric layer, it is preferred that 25 lower temperatures of about 15°C. to about 30°C. are used to improve the selectivity of the low-k dielectric material over the photoresist.

Depending on the composition of the cleaning composition, other selective etch ratios/rates are within the scope of the present invention. The selectivity and removal time can